

INTRODUCTION OF FLUORINE INTO COALS USING N-FLUOROBENZENESULFONIMIDE.

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INTRODUCTION

The selective introduction of fluorine into coals is under study as part of a program to define the chemical reactivity of coals through identification of reactive functional groups in the organic matrix of these solid fossil fuels. Recently, the number of reactive sites in coals as function of the strength of the organic indicator base has been determined by the C-methylation of O-methylated coals (1,2). The C-methylation was carried out by treatment of coal with carbanion bases and quenched with $^{13,14}\text{C}$ methyl iodide. The structural information derived from C-methylation of coals was limited to the number of reactive sites and an estimate of the methylene/methine site ratio (3). The generation of anions in coals is being repeated and quenched with N-fluorobenzenesulfonimide, 1, (4,5), a versatile electrophilic fluorinating reagent, in order to chemically attach fluorine to the reactive carbon site. The ^{19}F nucleus provides the mechanism, dipole-dipole coupling, to selectively observe the ^{13}C nuclei in its immediate vicinity through the use of ^1H - ^{13}C - ^{19}F double cross polarization (DCP)/MAS ^{13}C NMR. In conjunction with MAS ^{19}F NMR and CP/MAS ^{13}C NMR experiments, the goal is the definition of the reactive sites in sufficient detail to discover the chemical basis for the C-H acidity of the original carbanions.

RESULTS AND DISCUSSION

O-methylated Illinois #6 coal was prepared by using tetrabutylammonium hydroxide and methyl iodide (2,6,7). The different anions of O-methylated Illinois #6 coal were prepared using fluorenyl lithium, *n*-butyl lithium, and lithium diisopropyl amine (LDA), respectively, in THF. Each of the coal anions prepared by different bases was quenched with 1 at -78°C . The reaction mixture was slowly warmed to RT and stirred for an additional 15 hours under Argon. After addition of saturated NH_4Cl , the solution was diluted with 5% NaOH solution in order to destroy the excess 1. The coal was collected by filtration, and successively washed with water, 1N HCl, water, and ethanol. The coal was extracted exhaustively with THF using a Soxhlet extraction apparatus and then dried under vacuum for 18 hours at 100°C .

The ^{19}F NMR spectrum of the fluorinated coal prepared using fluorenyl lithium and 1 shows a strong resonance at -123 ppm and a less intense resonance around -170 ppm (Figure 1). These resonances correspond to tertiary and secondary alkyl fluorides, respectively. The spectrum also contains a poorly resolved broad resonance at -100 ppm. Associated with this center band are first and second order side bands that indicate a very large static linewidth

for this band. The linewidth and chemical shift of this band are the signature of *gem*-difluorocarbon species.

The difference spectrum between the CP/MAS- ^{13}C NMR spectra of the fluorinated coal prepared with fluorenyl lithium (Fig. 2a) and the O-methylated Illinois #6 precursor (Fig. 2b) is shown in Fig. 2c. Difference spectroscopy could show, in principal, the chemical shift reorganization due to the introduction of fluorine into the coal. In fact the difference spectrum is similar to the spectrum of fluorene, in the aromatic region, and indicates that the fluorenyl group is incorporated into the coal. The absence of the C(9) resonance of fluorene in the difference spectrum suggests the base is chemically attached to the coal network. The C(9) chemical shift will vary depending on the nature of the coal "substituent" at C(9), and will be distributed over a broad region. The remote aromatic carbons are less sensitive to the details of the bonding configuration at the sp^3 site. In control experiments it has been shown that physically absorbed fluorene can be completely removed by normal work-up procedures (Fig. 3). Hence, a fraction of the fluorenyl lithium reacts as a nucleophile and adds to O-methylated coal to give fluorenyl-coal linkages. These results support earlier work with $[9-^{13}\text{C}]$ -fluorenyllithium which show reagent-derived fluorene is chemically bound to the organic coal matrix (3).

The CP/MAS ^{13}C NMR of a fluorinated coal produced using *n*-butyl lithium and 1 reveals that the *n*-butyl group is also chemically grafted into the coal. This is evident from comparison of the aliphatic region of the resolution enhanced spectrum (upper trace in Fig. 4a) of this material with the corresponding region in the spectrum of the precursor coal (Fig. 2b). The resonance of the methyl group of the *n*-butyl moiety is quite insensitive to the nature of the attachment and appears as the sharp peak at 13 ppm. The spectrum in Fig. 2b does not show this resolved feature.

The CP/MAS ^{13}C NMR spectrum of the fluorinated coal produced using LDA and 1 is similar to that of the starting O-methylated Illinois #6 coal. The difference between these two spectra provides no evidence for *sec*-propyl amine resonances that would indicate nucleophilic addition of the base in the coal network.

While a necessary part of the background work to elucidate the chemical conversion occurring in the coal matrix the CP/MAS ^{13}C NMR spectra above do not reveal the fluorination chemistry the coal has undergone. This information is provided by the ^1H - ^{13}C - ^{19}F DCP/MAS ^{13}C NMR experiment (8). The DCP spectrum of the fluorinated coal prepared using fluorenyl lithium and 1 shows two kind of carbon resonances at 90-110 ppm and 150-170 ppm (Fig. 5). These resonances are assigned to alkyl fluoride carbons and aryl fluoride carbons, respectively. Aryl fluorides are formed by directed *ortho*-lithiation of activated aromatic rings (4).

The DCP/MAS ^{13}C NMR spectrum of the fluorinated coal prepared using *n*-butyl lithium and 1 (Fig. 4b) also shows aryl and alkyl fluoride resonance bands. The spectrum is similar to that of the fluorinated coal prepared with fluorenyl lithium and 1 (Fig. 5).

The DCP/MAS ^{13}C NMR spectrum of the fluorinated coal prepared using LDA and 1 shows only an aryl carbon resonance band.

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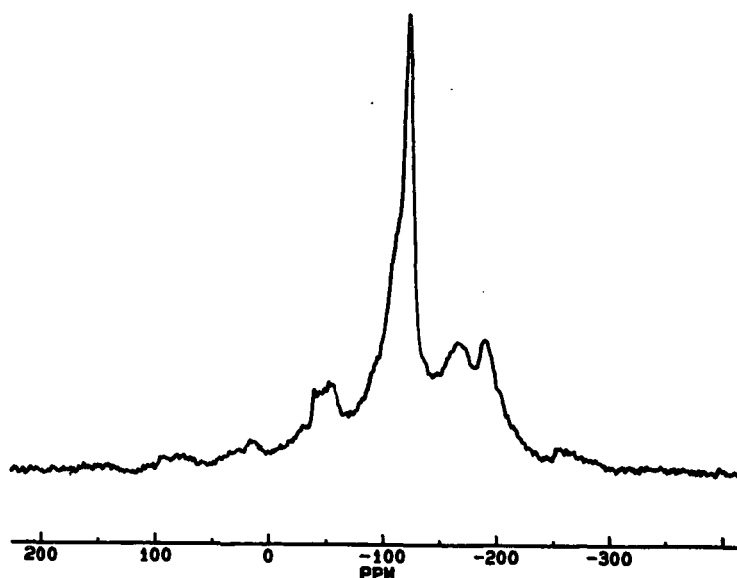


Fig. 1 MAS ^{19}F spectrum of a fluorinated coal by reaction of O-methylated Illinois # 6 coal with fluorenyl lithium and N-fluorobenzenesulfonimide.

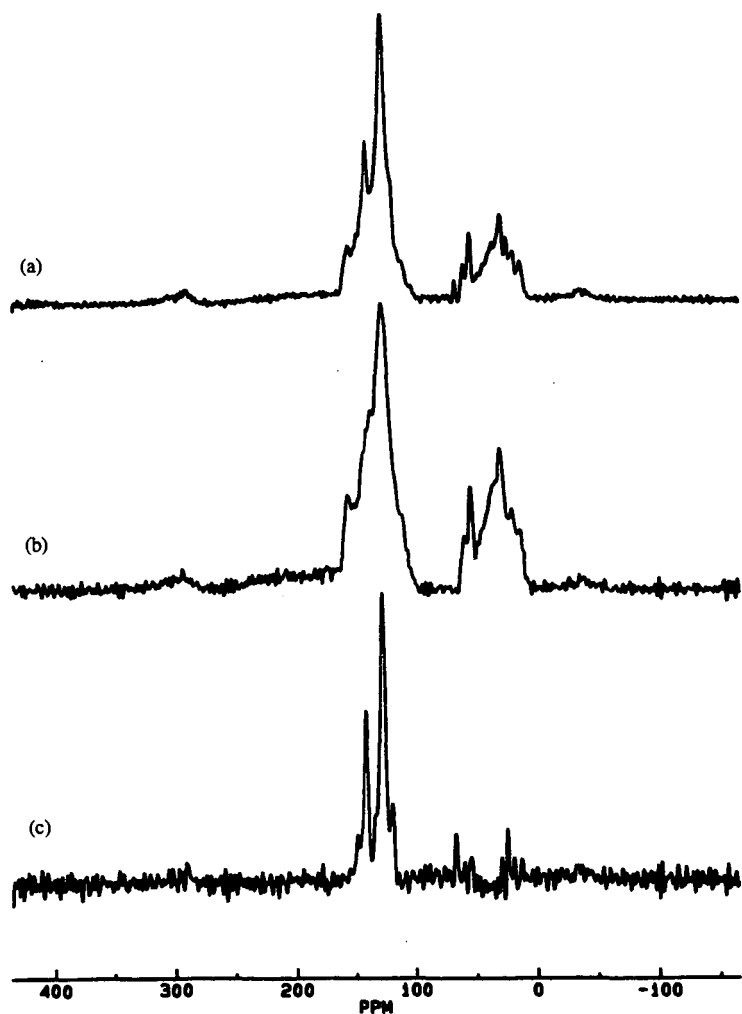


Fig. 2 (a) Resolution-enhanced CP/MAS ^{13}C spectrum of a fluorinated coal by reaction of O-methylated Illinois # 6 coal with fluorenyl lithium and N-fluorobenzenesulfonimide.
(b) Resolution-enhanced CP/MAS ^{13}C spectrum of O-methylated Illinois # 6 coal.
(c) Difference spectrum: (a) minus (b).

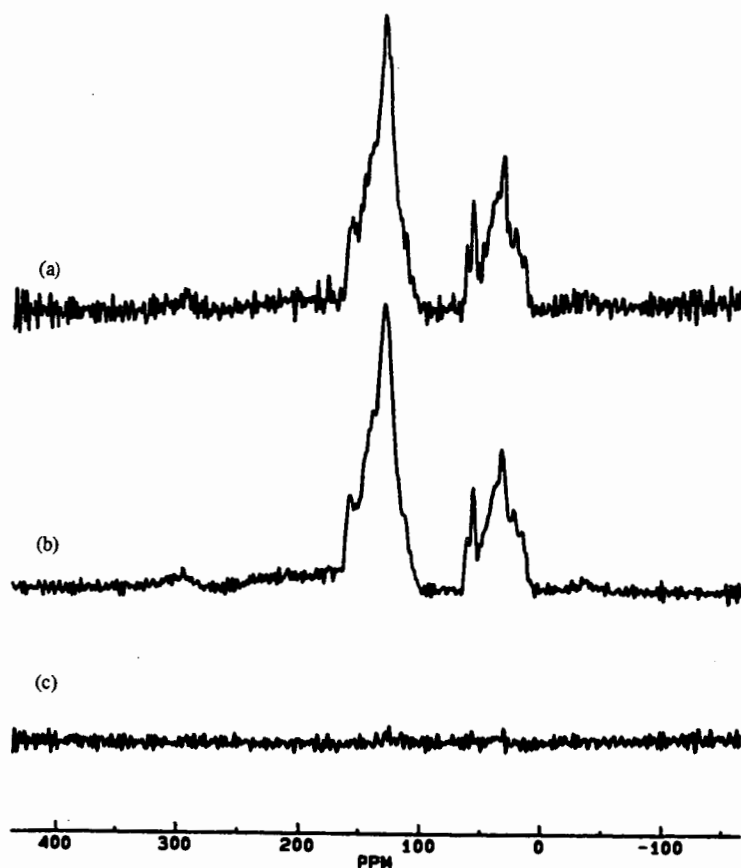


Fig. 3 (a) Resolution-enhanced CP/MAS ^{13}C spectrum of O-methylated Illinois # 6 coal which has been treated with fluorene and THF for 18hrs. and then successively washed with 5% NaOH, H_2O , 1N HCl, H_2O , and ethanol followed by vacuum drying for 18hrs at 100 $^{\circ}\text{C}$. (b) Resolution-enhanced CP/MAS ^{13}C spectrum of O-methylated Illinois # 6 APC coal. (c) Difference spectrum: (a) minus (b).

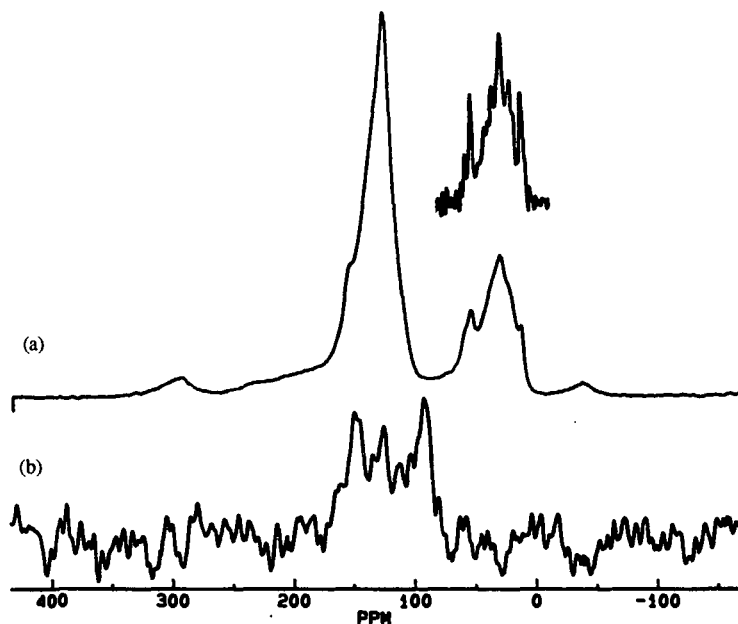


Fig. 4 (a) CP/MAS ^{13}C spectrum of a fluorinated coal by reaction of O-methylated Illinois # 6 coal with n-butyl lithium and N-fluorobenzenesulfonimide. The aliphatic region of the resolution-enhanced spectrum is plotted above the full spectrum.
(b) DCP/MAS ^{13}C spectrum of the same coal.

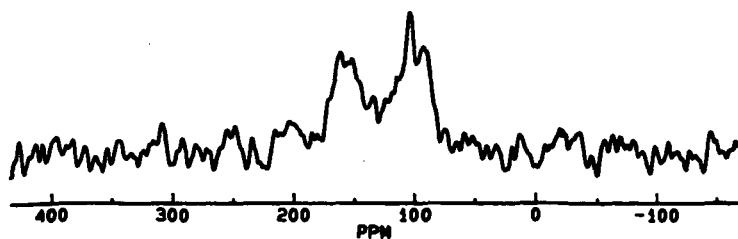


Fig. 5 DCP/MAS ^{13}C spectrum of a fluorinated coal by reaction of O-methylated Illinois # 6 coal with fluorenyl lithium and N-fluorobenzenesulfonimide.